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Combustion properties of torrefied willow compared with bituminous coals

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ABSTRACT

Thermal pre-treatment, or torrefaction, is a process that can improve the handling and grinding properties of biomass for combustion and co-firing. This paper compares the combustion properties of raw and torrefied Short Rotation Coppice Willow (SRC), with those of typical bituminous power station coals. The fuels were analysed using a number of standard fuel characterisation tests. Willow SRC was torrefied at 290 °C for two reaction times (10 min (short) and 60 min (long)). During torrefaction, longer reaction time promotes loss of nitrogen from the solid product. Chars were produced from the fuels under high heating rates up to 1000 °C and the char yields and nitrogen partitioning were determined. Results show that the nitrogen partitioning for both raw and torrefied biomass favours release of nitrogen into the volatiles during rapid pyrolysis. In contrast, rapid pyrolysis of the coals favours nitrogen retention in the char. The chars were subjected to thermogravimetric analysis-mass spectrometry (TGA-MS) combustion tests, which were used to calculate the char reactivities and fate of char nitrogen. The char reactivities follow the order coal char<torrefied willow char<raw willow char. The release of volatile-nitrogen species during char combustion occurs at higher temperatures for the torrefied willow chars compared to the raw willow chars due to their relatively lower reactivities. Like coal char, nitrogen is concentrated in the char (both raw and torrefied willow chars) as combustion proceeds and NO and N_2 species are released towards the end of char burnout.

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1. Introduction

The use of biomass for co-firing with pulverised coal for electricity production has been increasing rapidly in the UK. The amounts of biomass used in co-firing range from a few percentages up to 100% [1,2], but are typically <20% of the feedstock. Compared to coal, biomass has a lower energy density and it is harder to mill due to its fibrous nature; the latter can result in solid handling problems, particularly when firing in existing power stations. Torrefaction is a process that can improve both the energy density of biomass and its grindability properties [3–6]. In this process, biomass is heated at temperatures of <300 °C for a period of time, so that it undergoes mild pyrolysis. The resulting product is a solid which has properties intermediate between biomass and biochar. The properties of the torrefied biomass are very much determined by the process conditions, such as reaction time and more importantly the final temperature [3–7].

The combustion of pulverised coal has been studied extensively, prompted by the needs and importance of the coal-fired electricity industry [8–10]. The designs of the furnaces have been based on the use of pulverised coal, and the underpinning science is now well known, hence computer models have been developed which can track the combustion of coal particles and associated heat release [11–13]. In recent years, this understanding has been extended to the combustion of biomass, which has been co-fired with coal [13]. In the case of torrefied biomass, this level of knowledge has not been well developed yet, and there have not been any published data concerning large-scale industrial trials of the combustion of torrefied fuels. Some laboratory studies as well as CFD modelling studies have been made [3,5,14]. The combustion of solid fuels includes the main stages of pyrolysis to volatiles and char, and their subsequent combustion. Rates of volatile release and their composition are required to determine the rates of heat release. In the case of coal combustion, a significant amount of heat release comes from the char combustion and the complete burnout of the char is required to achieve high combustion efficiency. The combustion of biomass is slightly different from that of coal in that in a high temperature flame only 10–20% of the fuel remains as char which then burns out. Nevertheless, for both coal and biomass chars, the reactivity of the char, the porous structure and particle size, are important in determining the degree of burnout [15–17]. Additionally, if torrefied biomass was co-fired with coal instead of raw biomass, the combustion would be different because the torrefied fuel has different chemical properties to raw biomass (e.g. volatile and char ratio and composition, different heat contents, and reaction rates etc.). Some of these properties have yet to be established, and this paper seeks to do this.

The N-content in many biomass is usually less than 1% [18], lower than power station coals [8], and consequently NOx emissions during

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co-firing are expected to decrease. However, results on full-scale plant are mixed since burner configuration and firing condition are also critical in NOx control. However, the partitioning of fuel nitrogen between volatiles and char becomes important in developing the firing strategy to minimise NOx formation whilst maximising the extent of carbon burn-out. In these conditions, the role of the torrefied particle is complex since there are expected to be subtle changes from the behaviour of the (raw) biomass devolatilisation and char formation. These subtle changes are explored in the current paper. The behaviour of torrefied willow is examined by a number of techniques to further elaborate on the mechanism of combustion of torrefied biomass. Comparisons of N-partitioning and reaction rates are made with some published data for bituminous coal chars [19].

2. Experimental methods

2.1. Materials

The energy crop studied was short rotation coppice willow. The raw willow was ground using a Retsch cutting mill and sieved to produce two fractions studied, from which the fines (particles < 1 mm) were removed. The two particle size fractions used in torrefaction were: < 10 mm and > 20 mm (in length). The aspect ratios of these two particle size fractions (length to width) fell in the respective ranges of 5–8, and 2–5. The torrefaction procedure is outlined in Section 2.3. Chars were prepared from both the raw and torrefied willow samples as detailed in Section 2.4. Table 1 lists the willow samples and chars studied and their designations.

2.2. Fuel analyses

Prior to the proximate and ultimate analyses, the fuel samples were further milled using a RetschPM100 ball mill to reduce the particle size of the test sample to < 1 mm, in accordance with the test requirements. The ultimate analysis of the raw and torrefied willow fuels and their chars was performed using a CE Instruments Flash EA 1112 Series Elemental Analyser. The proximate analyses of the raw and torrefied fuels were conducted according to the methods in the European Standards CEN/TS 14775:2004 for moisture, CEN/TS 14774-1-3:2004 for volatiles, and CEN/TS 15148:2005 for the determination of ash. All the analyses were carried out in duplicates and a mean value is reported. The percent relative errors in H and C are better than 2%, whilst the percent relative error in N is better than 15%. This means that, for the calculation of the N-partitioning between char and volatiles, there is up to a 21% error in the values reported. All samples were stored under argon to prevent any uptake of atmospheric nitrogen during storage. The calorific value of the fuels was calculated from their elemental contents (% in dry basis) using Eq. (1) derived by Friedl et al. [20], namely:

$$\mathrm{HHV} = 3.55\mathrm{C}^2 - 232\mathrm{C} - 2230\mathrm{H} + 51.2\mathrm{C} \times \mathrm{H} + 131\mathrm{N} + 20{,}600\left(\mathrm{kJ\ kg}^{-1}\right). \quad (1)$$

Table 1
Sample designations for the materials used and generated in this study.

Sample designations	Material and preparation conditions
10 W	Raw willow, particle size < 10 mm
20 W	Raw willow, particle size > 20 mm
10 T-10 min	10 W torrefied, 10 min reaction time
20 T-60 min	20 W torrefied, 60 min reaction time
10 W char	Char from 10 W
20 W char	Char from 20 W
10 T-10 min char	Char from 10 T-10 min
20 T-60 min char	Char from 20 T-60 min

2.3. Torrefaction

Full details of the torrefaction procedure are given in Bridgeman et al. [7]. Briefly, between 50 and 100 g of dried sample is placed into the reactor tube under a N_2 flow of 1.0 L min^{-1} at STP. The samples were first heated at 10 °C/min to 150 °C and held for ~50 min, before being taken to a final temperature (T_{max}) of 290 °C, at a heating rate of 10 °C/min and held at this temperature for either 10 min or 60 min.

2.4. Char preparation

After torrefaction of the two particle size fractions (< 10 mm and > 20 mm), both the raw biomass and the torrefied samples were milled to reduce the particle size to < 90 μm using a Spex 6770 freezer/mill prior to char preparation. High heating rate chars were then prepared from both the *raw biomass* and the *torrefied* counterparts (four samples in all). The chars were prepared using a CDS 2000 Pyroprobe. The pyroprobe was inserted into a CDS 1500 interface, which was operated at a temperature of 250 °C. A flow of helium was fed into the interface to provide an inert atmosphere. For each run, a total of approximately 10–15 mg of sample was placed into a quartz tube and held in position using quartz wool plugs. After insertion into the interface, a period of time was allowed to pass in order to purge any air from the chamber. The sample was then subjected to a nominal programmed heating rate of 10,000 °C s^{-1} and held at 1000 °C for 30 s, however the actual heating rate experienced has been estimated as 1000 °C s^{-1}. The pyrolysis process was replicated for each sample in excess of 50 times and the samples combined to produce sufficient sample mass for the physical and chemical analysis.

2.5. Characterisation of the chars by simultaneous thermal analysis-mass spectrometry (STA-MS)

The char reactivities were determined in two ways, both using a Netzsch STA 449 Jupiter. Firstly, for all chars, by temperature programmed oxidation in 12.5% O_2/He, and secondly, by isothermal combustion for the 20 W char and the 20 T-60 min char, also in O_2/He. This was to check for suitability of temperature programmed thermal analysis for obtaining the oxidation kinetics. In the temperature programmed oxidation experiments, the samples (< 10 mg) were heated at 10°/min and products were analysed by on-line mass spectrometry as described below. In the isothermal oxidation experiments (~5 mg) chars were heated in helium to a set point temperature(in the range of 360–420 °C), and then the gas supply was switched to 12.5% O_2/He. In both sets of experiments, the apparent first order rate constants were estimated as a function of temperature such that Arrhenius parameters could be obtained.

The char nitrogen evolution during combustion was studied simultaneously via an on-line Netzsch QMS 403C Aëolos quadrupole mass spectrometer for the analysis of the evolved gases. The species evolution curves were used to compare the release of nitrogen species from the different chars. The species monitored by mass spectrometry were m/z 14 (N_2^{2+} and CO^{2+}), m/z 27 (HCN + tail end of m/z 28 signal), m/z 28 (dominated by $^{12}C^{16}O$), m/z 30 (NO + $^{12}C^{18}O$), m/z 43 (HCNO + tail end of m/z 44 signal), m/z 44 (dominated by $^{12}C^{16}O_2$), m/z 46 (NO_2 + $^{12}C^{16}O^{18}O$), and m/z 52 (C_2N_2). In order to correct for the interferences and detector resolution at m/z 14, 27, 30, 43, 46, an identical experiment was performed with pure graphite (which of these species produces only CO and CO_2 upon combustion). From the signals measured at these m/z values, correction factors were determined and applied to the data from the char experiments. This enabled correction of these signals for the different carbon isotopes, such that the N-species evolution profiles could be generated. Details of this technique can be found in Darvell et al. [21–23].

2.6. Surface area measurements

The BET surface areas of the samples (<90 μm)were determined using a Quantachrome Instruments Nova 2200e automated surface area and porosity analyser in adsorption mode, with proprietary NovaWin software used to perform the data acquisition and processing. The adsorbate gas was nitrogen (BOC Zero Grade), whilst the carrier gas was helium (BOC CP Grade). Six values of nominal values of P/P^0 (adsorbate partial pressure) were used to construct the multipoint BET plot, from 0.05 to 0.30. The analysis of the raw willow sample (20 W) was conducted as received, whilst for the torrefied sample (20-T 60 min) and chars (20 W char and 20-T 60 min char) these measurements were carried out after out-gassing under a constant flow of nitrogen (125 °C, 2 h).

3. Results

3.1. Properties of the fuels and chars

The designations of the samples studied in this work are given in Table 1. Full characterisation of the two size fractions of the raw (as received) willow and their torrefied counterparts are given in Bridgeman et al. [7]. The char yields obtained from the pyrolysis of these four samples are given in Table 2, which also gives information about the N-partitioning which is discussed in Section 3.2.2. Torrefaction causes partial devolatilisation, and hence torrefied fuels have a reduced volatile content; similarly, torrefied fuels also give higher char yields. The ultimate analysis of the fuels and their corresponding chars are shown in Table 3 on a dry ash-free basis. It is to be observed that the weight percent nitrogen increases in the chars relative to the parent fuel, and there appears to be an influence of prior torrefaction on the weight percent nitrogen in the char.

The surface area of the raw willows (10 W and 20 W) were measured as $3.9 \pm 0.8\ m^2/g$, and the surface areas of the torrefied willows were $3.4 \pm 0.4\ m^2/g$. Chars prepared from the willow had a surface area of $157\ m^2/g$ whilst 20 T-60 min torrefied willow had a surface area of $270\ m^2/g$. Thus we see very little change in surface area with torrefaction at 290 °C for 60 min. However, both chars display a development of porosity and surface area, and this is higher for chars prepared from the torrefied fuels.

3.2. Characterisation of chars by TGA

3.2.1. Char reactivity

Studies of the oxidative reactivity of the chars were made, and the resultant burning profiles are shown in Fig. 1. The apparent first order reactivity of the chars from willow and torrefied willow was determined from the weight loss with time curves, assuming the apparent first order rate constant, $k_c' = 1/w_t \cdot dw/dt$ (reaction rate constant method). This is also compared with a method used previously by us for pyrolysis kinetics [24], and originally developed by Senum and Yang [25]. The kinetic parameters calculated for the fuel chars are given in Table 4. It is interesting and intriguing to note that the weight loss curves differ markedly between 20 T-60 min char and the chars from the two raw willow size fractions, i.e. the char reactivity differs depending on if it is derived from a raw biomass (higher reactivity char) or a torrefied biomass (lower reactivity char). In fact, the reactivity follows the order 10 W char > 20 W char > 10 T-10 min char > 20 T-60 min. This is explored further in the discussion section together with a comparison with coal char reactivity.

Table 2
Char yield and nitrogen partitioning during devolatilisation of raw and torrefied willow.

Parameter	10 W	20 W	10 T-10 min	20 T-60 min
N in fuel (wt.% daf)	0.58	0.58	0.71	0.52
N/C in fuel	0.010	0.010	0.011	0.007
Char yield (wt.% daf)	14.8	15.3	22.5	28.6
Fuel-N in char (%)	41	42	41	44
Fuel-N in volatiles (%)	59	58	59	56
N/C in char	0.017	0.016	0.014	0.009

Table 3
Ultimate analysis of fuels and chars.

Fuels and chars	C (wt.%) daf	H (wt.%) daf	N (wt.%) daf	O^a (wt.%) daf	Ash (wt.%) dry	HHV ($MJ\ kg^{-1}$) dry
10 W	48.6	6.4	0.6	44.4	2.0	19.4
20 W	49.3	6.3	0.6	43.9	1.6	19.0
10 T-10 min	56.5	6.2	0.7	36.6	2.1	22.4
20 T-60 min	60.3	5.8	0.5	33.3	1.8	24.0
10 W char	80.9	2.2	1.6	15.2	12.0	n.d.
20 W char	84.6	2.3	1.6	11.5	14.0	n.d.
10 T-10 min char	79.9	2.1	1.3	16.7	12.0	n.d.
20 T-60 min char	80.2	1.9	0.8	17.1	9.2	n.d.

n.d. not determined.
[a] By difference.

3.2.2. Nitrogen partitioning and char-nitrogen conversion

The nitrogen partitioning calculated by a mass balance from the nitrogen contents of the fuel and its corresponding char is given in Table 2. For comparison purposes, the nitrogen partitioning for a selection of traded bituminous coals studied previously [19] is also shown in Table 5. The effect of torrefaction on the nitrogen content of the chars can be seen clearly in the data shown in Table 2, where the N/C ratio increases for all the chars compared with the parent fuel. Chars prepared from torrefied willow (10 T-10 min and 20 T-60 min) show a lesser degree of nitrogen enrichment than the chars prepared from the raw biomass. Hence it appears that longer torrefaction reaction times result in more volatile-N during pyrolysis and char formation. However, the nitrogen partitioning calculations given in Table 2 show no discernible difference between the torrefied willow fuels and the raw willow feedstock fuels. For all fuels analysed, approximately 40% of the fuel nitrogen remained in the char whilst 60% entered the volatile fraction. Comparing these results to those obtained for the bituminous coals (Table 5), it is seen that the split of fuel nitrogen for coal is near to 60% in the char, and 40% in the volatiles, with the exception of Thoresby coal, which shows a higher char-N release. Additionally, some of the nitrogen compounds

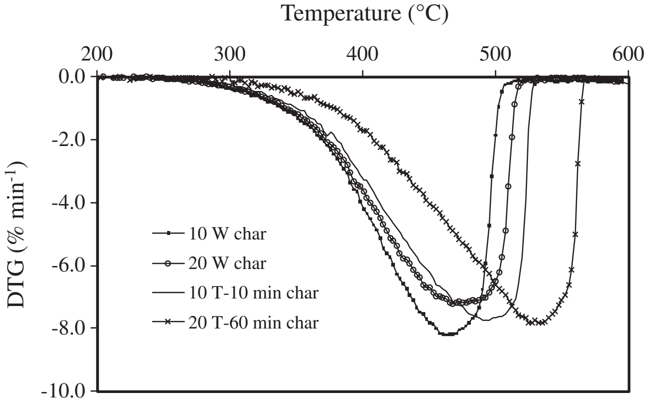

Fig. 1. DTG plots for the temperature programmed combustion at 10 °C min^{-1} of chars from raw and torrefied willow in 12.5% O_2 in He.

Table 4
Apparent first order combustion reactivity of the chars from raw and torrefied willow.

Fuel	Temperature Programmed combustion				Isothermal combustion		Rate constant at 400 °C, k_{400}		
	Senum–Yang		Reaction rate constant method		Reaction rate constant method		Senum–Yang	Reaction rate constant method	
	E ($kJ\ mol^{-1}$)	A (s^{-1})	E ($kJ\ mol^{-1}$)	A (s^{-1})	E ($kJ\ mol^{-1}$)	A (s^{-1})		TPO	Isothermal
10 W char	88.1	5680	84.6	3219			0.000825	0.000874	
20 W char	84.1	2590	81.7	1735	83.7	1634	0.000769	0.000791	0.000791
10 T-10 min char	81.6	1310	83.1	1629			0.000608	0.000578	
20 T-60 min char	83.7	940	87.4	1971	93.8	5336	0.000300	0.000324	0.00028
Asfordby coal char					195	1.01×10^{11}			7.39×10^{-5}
Thoresby coal char					185	3.38×10^{9}			1.48×10^{-5}
Pittsburgh 8 coal char					188	7.43×10^{9}			1.90×10^{-5}
S Brandon coal char					198	1.94×10^{10}			8.31×10^{-6}

released during char combustion were detected by mass spectrometry and some typical evolution profiles are shown in Fig. 2. There is a clear change in the emission profiles due to the pre-treatment of the fuel, which will be discussed further in the next section.

4. Discussion

4.1. General comments

The combustion of pulverised bituminous coals involves the steps of devolatilisation followed immediately by char combustion with very little overlap of the processes. In the case of coal, anisotropic cenosphere particles may be formed, but the devolatilisation stage is completed with little volatile material retained in these char particles. In the case of torrefied biomass, the pre-treatment process itself is shown to influence the subsequent combustion. Torrefaction involves the partial mild pyrolysis of biomass particles and then the product is slowly quenched with the result that the product contains slightly lower volatiles than the raw biomass particle and, whilst there may be some pore development in torrefaction, this is limited. This is demonstrated by the surface area measurements of the raw and torrefied biomass of 3.9 ± 0.8 m^2/g and 3.4 ± 0.4 m^2/g respectively. The resultant solid torrefied product has an increased carbon content and has developed a hydrophobic nature [26,27]. Both these properties depend on the torrefaction conditions. In the experiments summarised here, typical torrefaction conditions were studied, and it was found that a small variation in the particle size does not influence the carbon yield for biomass. The mass and energy yields for the torrefaction process for the willow samples have been reported previously [7]. The mass yield for sample 10 T-10 min was ~82%, whilst for sample 20 T-60 min was ~67%. These resulted in energy yields of ~90% and ~78%, respectively. Hence a greater mass loss was observed with a longer reaction time. A further factor in mass and energy yield in torrefaction is the content of the potassium, which has an effect on the decomposition rates of the solid fuels [7]. Because of the low temperatures used in torrefaction, the potassium in the biomass will be retained in the remaining solid after torrefaction. The many studies of the pyrolysis step of coal [28] and biomass [24] have been extensively reported. The rate of decomposition of the biomass during the torrefaction process is consistent with the kinetic data for the first order pyrolysis of wood given in the compilation by Saddawi et al. [24]. Thus, for willow torrefied at a typical temperature of 290 °C, the torrefaction rate constant is $2.4\times10^{-3}\ s^{-1}$. When chars are prepared from the torrefied or the raw biomass material, some differences are observed as highlighted in Table 3. In the case of torrefied biomass, their chars have a higher carbon content than chars prepared from raw biomass.

Table 5
Nitrogen partitioning during devolatilisation of some bituminous coals. Data calculated from Jones et al. [19].

Parameter	Asfordby	Thoresby	Pittsburgh 8	South Brandon
N in fuel (wt.% daf)	1.55	1.86	1.64	1.77
N/C in fuel	1.64	1.94	1.70	–
Char yield (wt.% daf)	50.1	67.3	47.6	44.3
Fuel-N in char (%)	66	83	59	54
Fuel-N in volatiles (%)	34	17	41	46
N/C in char	1.88	2.10	1.89	2.03

4.2. Reactivity of chars from coals, biomass and torrefied biomass

The overall combustion time for a biomass or torrefied biomass particles depends on the size of the particle and thus the heating-up time followed by the rate of devolatilisation and heterogeneous char combustion. From the mass loss curves in Fig. 1, it can be observed that there is a difference in reactivity for chars prepared from raw vs. torrefied biomass. The corresponding apparent first order Arrhenius parameters are given in Table 4. Here, a comparison is given of the different methods for evaluating these parameters. There is an indication that slightly higher activation energies are extracted from isothermal oxidation compared to temperature programmed oxidation (TPO). The reaction rate constant method (both from TPO and isothermal experiments) yields the highest activation energy associated with char from the most torrefied fuel (20 T-60 min char). From the rate constant calculated at 400 °C we see that reactivity at this temperature follows the order 10 W char > 20 W char > 10 T-10 min char > 20 T-60 min char. The proximate analysis of both raw and torrefied willows has been reported previously [7], and the volatile content was found to decrease from ~74% (as received) in the raw biomass to ~72% for 10 T-10 min and ~66% for 20 T-60 min. During char formation at high heating rate, there is a rapid escape of volatiles from the biomass particles with concomitant development of the porous structure. One explanation of the lower reactivity of chars from torrefied biomass compared to chars from raw biomass is that the lower volatile content of the former, together with the different composition of volatiles (bigger fraction of higher molecular weight material), results in a char with less developed porosity, and hence lower reactivity. However, the char produced from the torrefied willow was found to have a higher surface area than the char from the raw willow (270 m^2/g compared to 157 m^2/g), so it is clear that the pore structure has developed more, not less, in the char from the torrefied material. Hence the lower reactivity of torrefied biomass char compared to raw biomass char is not related to a lower surface area.

The lower reactivity of torrefied biomass char compared to raw biomass char has also been observed under flame conditions. One of our previous studies of combustion of raw and torrefied willow

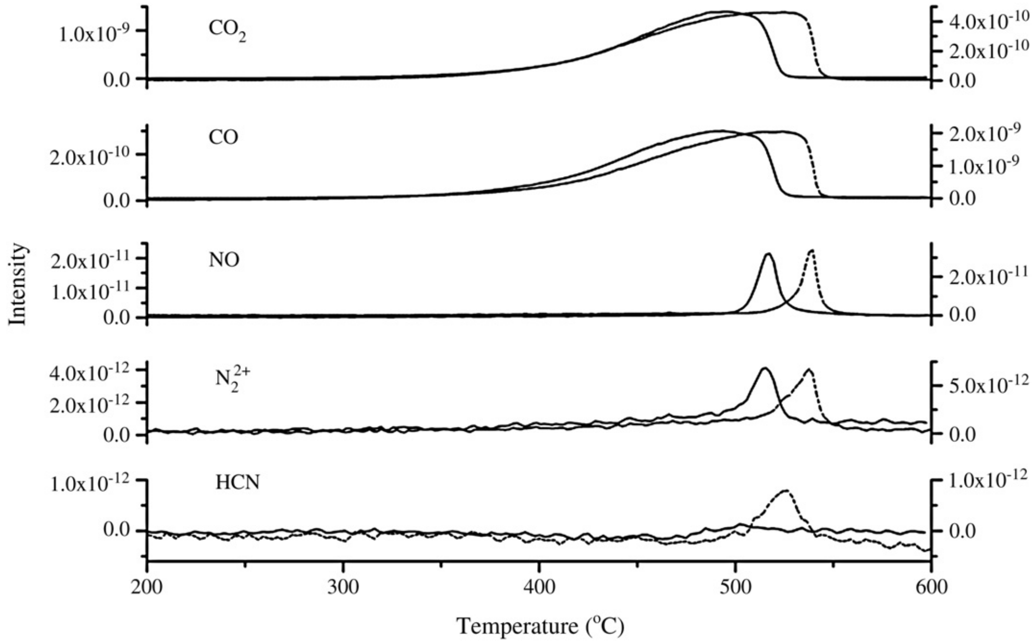

Fig. 2. Typical N-species evolution during temperature programmed combustion at 10 °C min^{-1} of chars from raw and torrefied willow in 12.5% O_2 in He, where (—) 10 W char and (---) 10 T-10 min char.

particles (1–3 mm) in flames [4], showed that the duration of the char combustion stage for particles of raw willow is shorter than for particles of torrefied willow. Some of these results are reproduced in Fig. 3, which shows the difference in char combustion rates for raw willow and torrefied willow (prepared to a final temperature of 290 °C, with a reaction time of 30 min). It is clear that over the size range studied experimentally, the torrefied char particles burn more slowly but the two curves are converging as the particle size gets smaller.

Fig. 3 can be related to pulverised fuel combustion by converting to an equivalent spherical particle diameter: A 1 mg particle equates to a particle of 828 μm radius (assuming a density of 420 kg m^{-3}) whereas a 0.1 mg particle (obtained by extrapolation) would correspond to a 384 μm radius particle. Raw biomass is notoriously difficult to reduce to a small particle size, whilst there is substantial evidence that milling of torrefied biomass results in particles with much smaller size distributions [7]. Consequently, in practical terms the decreased char reactivity of torrefied biomass may be countered in pf combustion by the ability to achieve smaller particle sizes, and hence carbon burn-out of raw versus torrefied biomass under power station conditions may be similar as previously suggested [14]. However, the difference in reactivity is intriguing and is worthy of further study. It is also notable that the difference in reactivity is only observed under conditions of rapid heating during the devolatilisation stage. Additional work [29] has illustrated that chars prepared from raw and torrefied biomass at slow heating rate are essentially the same.

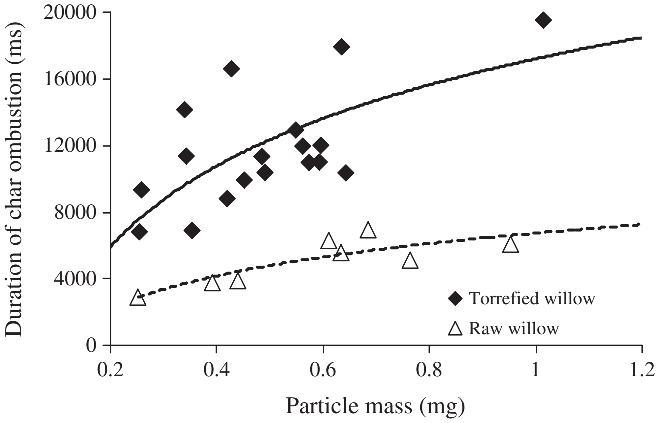

Fig. 3. Duration of the char combustion stage for single particles of raw willow and torrefied willow (T_{max} = 290 °C and 30 min reaction time).
Figure modified from Bridgeman et al. [4].

The combustion of coal chars has been well studied over a wide temperature range with most studies being undertaken at <1200 K, although some have been made at flame temperatures [16,30,31]. Both chemical and intrinsic reactivities have been investigated. Porosity is known to develop as combustion proceeds, but for modelling purposes average values of surface areas are adopted [11,32]. In comparison, the combustion of biomass chars is less researched. Di Blasi [33] has summarised the state of knowledge with regard to the chemical reactivities of lignocellulosic chars, but in order to obtain intrinsic reactivities it is necessary to determine the surface area at the same instant in time. This has proved to be difficult, resulting in values that differ by an order of magnitude. In Table 4 chemical reactivities are reported and compared with those for coal chars prepared in a drop tube furnace [19] (also at high heating rate). Their corresponding chemical reactivities estimated at 400 °C are also included for comparison purposes. As noted above, the different methods of extracting the apparent first order kinetics of oxidation of the chars yield similar values, and predict the same order of reactivity for the different fuels. Chars from the torrefied willow present comparable activation energies to the chars from raw biomass, but chars from both torrefied and raw biomass have lower activation energies than coal chars.

The difference in activation energies between biomass chars and coal chars results in an interesting consequence: At 400 °C, coal chars present much lower reactivities (an order of magnitude lower) than torrefied and raw biomass chars, however at 500 °C (not shown), the estimated reactivities of coal chars and biomass chars are of the same order of magnitude. The temperature of 500 °C would be close to the transition from Zone I to Zone II kinetics, expected as the fuel particle nears the end of combustion and the particle temperature starts to drop. In reality, there will be significant annealing of the char particles with subsequent loss of reactivity, and the extent of char deactivation will depend on the initial char structure and carbon structure. Bituminous coals produce anisotropic coke-like particles for which annealing and loss of porosity and reactivity at high temperature are well documented. Biomass produces isotropic porous chars which will retain more of their porosity during annealing [34].

Intrinsic reactivities are plotted in Fig. 4, together with some appropriate data for bituminous coals, which were taken from Jones et al. [19]. Similar data for bituminous coals can be found in the literature, for example, Tsai and Scaroni [35] (chemical reactivities) and Chan et al. [17] (intrinsic reactivity). It is seen that the biomass char is more reactive than the torrefied biomass char. The experimental data for the biomass char is consistent with the compilation of data for a range of different biomass given by Di Blasi [33]. Of course, both raw biomass chars and torrefied biomass chars are more reactive than the chars from bituminous coals (note—Asfordby is an unusually reactive bituminous coal char), but it is interesting that the torrefied biomass char moves closer to the intrinsic reactivity of the coal chars, as shown by the solid line from [19].

There has been a great deal of debate about how reactivities (measured at low temperatures) translate into high temperature furnace applications. In pf (small particle) combustion, it is considered that particles will be in Zone II in the initial stages of char combustion which will change to Zone I as burnout nears completion. Thus, low temperature studies are relevant for later stages of burnout. However, what they cannot capture is the differences in annealing experienced by coal chars [11,17] and biomass chars at high temperature [34], and also the changes, through evaporation, in metal concentrations in char with burn-out at high temperature. This latter factor will be particularly relevant for biomass with high concentrations of inherent catalytic potassium salts. Because of these difficulties, low temperature kinetics are often extrapolated to high temperature flames [36], where the limited evidence suggests that biomass chars still burn faster than coal chars. For example, Levendis et al. [37] studied single particle combustion of a range of coals and bagasse and found the average char combustion duration for 40–90 μm particles of bagasse to be nearly four times faster than bituminous coal chars.

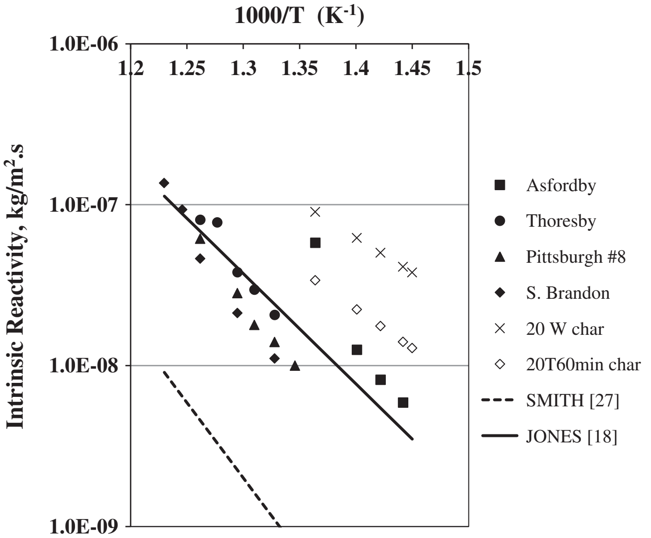

Fig. 4. Intrinsic reactivity of chars from raw willow and torrefied willow in comparison with coal chars (from [19]); reactivity has been normalised to 101 kPa O_2, and per unit surface area in m^2/kg. Bold line (Jones) is from [19] and dashed line is from Smith [30].

4.3. The release of N-compounds and formation of NO

The organic nitrogen in biomass is in the form of linear and cyclic N-compounds [38,39]—mostly in the form of proteins [38,40]. Two main reaction routes for the decomposition of protein nitrogen have been proposed in the literature from pyrolysis studies of nitrogen-containing model compounds and bark [40]. One route leads to NH_3 and the other to the formation of HCN, with their corresponding reactions competing in the solid phase only. In the first route, the formation of NH_3 simultaneously leads to char formation, whilst the second route leads to the formation of volatile cyclic amides, which in turn may result in HCN or HNCO upon cracking. From Fig. 5, it can be noticed that the torrefaction reaction time appears to have an effect on the nitrogen partitioning, with shorter reaction times (Fig. 5(a)) favouring the retention of nitrogen in the torrefied biomass (100% remaining in the solid), whilst longer reaction times (Fig. 5 (b)) encourage the loss of nitrogen in the volatiles despite the larger particle size used (60% retained in the torrefied product). This can be explained since torrefaction is a mild pyrolysis process and it has been demonstrated that low temperatures and short residence times encourage the retention of nitrogen in the remaining solid [41].

Results of rapid pyrolysis of the raw and torrefied willow are given in Table 2 and Fig. 5(a) and (b). Here, results of N-partitioning are quite similar for the raw and torrefied biomass, with a larger fraction of nitrogen evolving with the volatiles than being retained in the char (~41–42% N retained in char from raw willow, and 41% and 44% N retained in the char from 10 T-10 min and 20 T-60 min respectively). Note that in the case of the torrefied fuels there was an initial loss of nitrogen due to the torrefaction process; here we have calculated char-N/torrefied fuel-N, so the small loss of nitrogen during torrefaction is not included in the partitioning data for the torrefied fuels. This preferential loss of nitrogen in the volatiles for the torrefied fuels is beneficial in terms of nitrogen emissions, however this effect is only significant when the longer reaction time is used (i.e. 20 T-60 min), and this can be observed more clearly from the balance shown in Fig. 5. In contrast, from the N/C ratios listed in Table 5 and the data shown in Fig. 6 it can be observed that the nitrogen is preferentially retained in the coal chars during rapid pyrolysis (54–83% N retained in the char for the different coals). Note, that data is presented to three significant figures in Figs. 5 and 6 in order to prevent rounding errors.

Typical gas evolution profiles are shown in Fig. 2. It can be observed that the release of CO_2, CO, and volatile-nitrogen species during char combustion occurs at higher temperatures for the torrefied fuels compared to the raw fuels. This was expected as the chars from the torrefied fuels are less reactive due to increased cross linking [42], and possibly a less porous structure as discussed earlier. This distinction is of slight importance for staged burners since much of torrefied fuel will burn in the later stages, although this will depend on the fineness of the particles. The evolution profiles show that, like coal char [22], the nitrogen species are not evolved at the same rates as the CO and CO_2 from combustion. Rather, they concentrate in the char during combustion, and are evolved towards the end of combustion. HCN (when detected) evolves earlier than NO and N_2. The conversion of the char-nitrogen to NO and other N-species during combustion is listed in Table 6. These numbers are semi-quantitative in that they can be used in a comparative way between different samples. It is clear that, whilst torrefaction has an effect on the N-content it does not significantly influence the formation of NO when the fuel chars are combusted in the TGA. However, it is to be noticed that some HCN was detected from the combustion of the 10 T-10 min char, and more N_2 is detected from the combustion of the 20 T-60 min char. A possible explanation to the former could be that since the shorter torrefaction residence time leads to higher nitrogen (and tar) retention in the resultant fuel, the N-compounds in the torrefied biomass have tended to cyclise and some HCN may be formed upon cracking of larger fragments during char combustion. It must be noted that HCN has been identified as a direct product from coal char combustion, eventually leading to the formation of N_2O [23]. HCN was not detected in the 20 T-60 char, but this may be due to the lower N-content of that solid. N_2O cannot be detected here because of the high CO_2 signal at the same mass, m/z 44. In heterogeneous char combustion, N_2O is thought to arise from the reduction of NO (a primary product) on the char, but in the case of coal char combustion is also sensitive to O-content, N-content, air–fuel ratio and mineral matter [21,43–46]. The N_2O yield appears to be dependent upon the oxygen concentration in the char [21] and it has also been observed that a higher O-content char favoured N_2 production over N_2O. Thus, whilst some N_2O is expected as a product from the combustion of the raw and torrefied willow chars, their high oxygen content will favour N_2 over N_2O release. The present work supports this observation, and chars from the torrefied willow, which have slightly higher oxygen content than chars from the raw willow, produce slightly higher conversions of char nitrogen to N_2 during combustion.

5. Conclusions

The combustion properties of raw and torrefied willow have been investigated and compared to those of typical bituminous coals. Chars have been produced from the raw and torrefied biomass fuels, and the char yields and nitrogen partitioning determined. During torrefaction, longer reaction time promotes loss of nitrogen from the solid product—in this case 40% of the nitrogen was lost during torrefaction for a reaction time of 60 min compared to no measureable loss for a reaction time at 10 min. Results show that the nitrogen partitioning for both raw and torrefied biomass favours release of nitrogen into the volatiles during rapid pyrolysis (about 55–60% fuel-N released into the volatiles). In contrast, rapid pyrolysis of the coals favours nitrogen retention in the char (about 40% N released

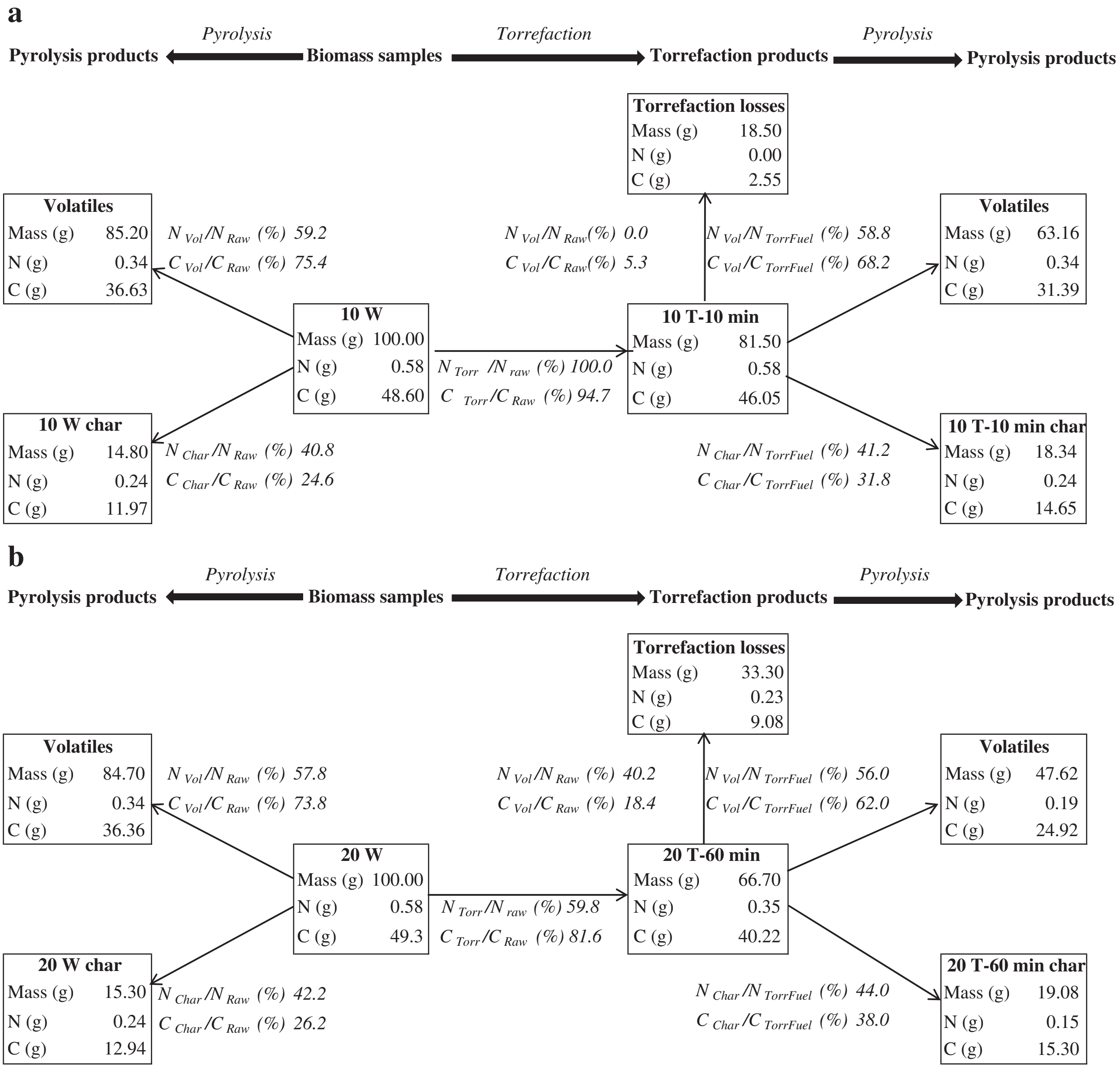

Fig. 5. Diagram showing the distribution of nitrogen and carbon throughout the process leading to combustion for (a) sample 10 W, (b) sample 20 W.

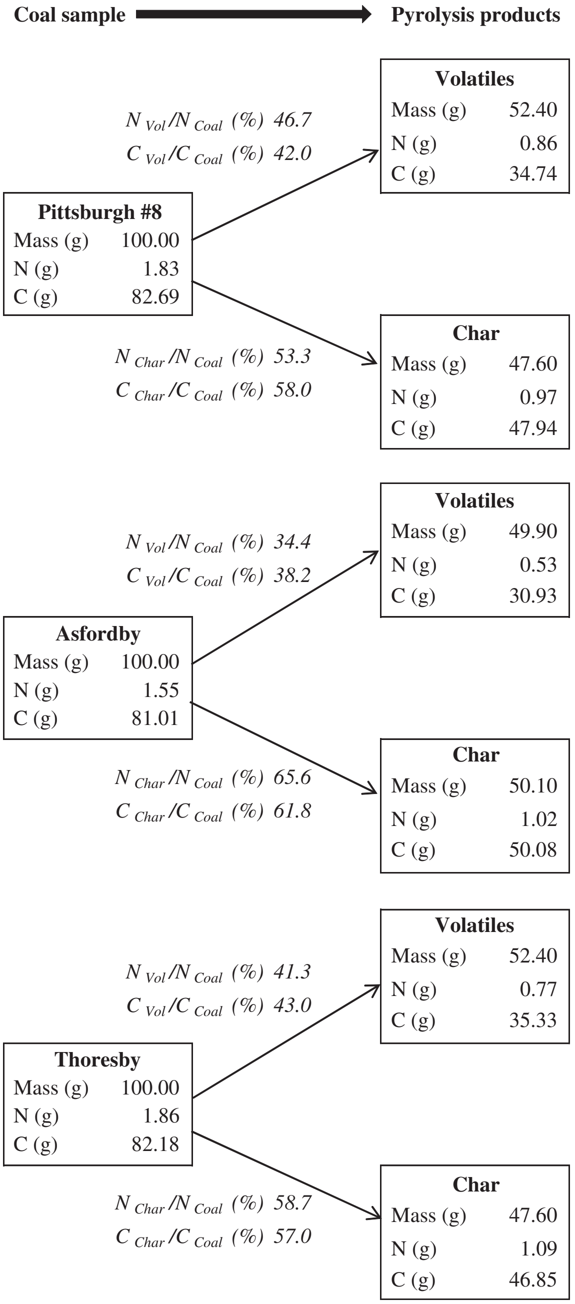

Fig. 6. Diagram showing the distribution of nitrogen and carbon during the pyrolysis of bituminous coal samples.

into the volatiles). Of the three types of fuel (bituminous coal, torrefied willow and raw willow) the char reactivities follow the order: coal char<torrefied willow char<raw willow char. As the torrefied willow chars are less reactive than the raw willow chars, the release of volatile-nitrogen species during char combustion occurs at higher temperatures. Like coal char, nitrogen is concentrated in the char as combustion proceeds and NO and N_2 species are released towards the end of char burnout. The high O-content of the biomass char appears to favour N_2 release during combustion.

Table 6
Nitrogen compounds released during char combustion of the chars.

N-species/char-N	10 W char	20 W char	10 T-10 min char	20 T-60 min char
N_2/N	0.37	0.38	0.42	0.48
NO/N	0.20	0.14	0.17	0.17
NO_2/N	n.d.	n.d.	n.d.	n.d.
HCN/N	n.d.	n.d.	0.01	n.d.
HCNO/N	n.d.	n.d.	n.d.	n.d.
Total	0.57	0.52	0.60	0.65

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